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03 Solutions

Introduction

Definition of Solution

When two or more chemically non-reacting substances are mixed together to form a homogeneous mixture is called as a solution.

When the solution is composed of only two chemical substances, it is termed as binary solution, similarly, it is called ternary and quaternary if it is composed of three and four components respectively.

For binary solution: Solution = solute + solvent

- Generally, the component present in lesser amount than the other component in solution is called as solute.
- Generally, the component present in greater amount than all the other components is called as solvent.
- Physical state of solvent and solution is same.

Solution	Solute + Solvent	
	(B)	(A)
moles	n	N
mass	w(g)	W(g)
molar mass	m	M
mole fraction	x_B	x_A

Ex.1: In a syrup (liquid solution) containing 60 g sugar (a solid) and 40 g water (a liquid) same aggregation as solution water is termed as the solvent.

Ex.2: In a solution of alcohol and water; having 10 mL alcohol and 20 mL water, water is solvent and alcohol is solute.

- On the basis of amount of solute, solutions can be classified in two ways.

(a) Dilute Solution

A solution in which relatively a small amount of solute is dissolved in large amount of solvent is called a dilute solution.

(b) concentrated Solution

A solution in which relatively a large amount of the solute is present in the given amount of solvent is called a concentrated solution.

Concentration Terms

(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)
Normality (N)	**Molarity** (M)	**Formality** (F)	**Molality** (m)	**Strength of a Solution** (S)	**Concentration in terms of percentage** (w/W, v/V, w/V)	**Parts Per Million** (ppm)	**Mole Fraction** (X)

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(a) Normality (N)

The number of equivalents or gram equivalents of solute present in one litre of the solution is known as normality (N) of the solution.

$$\text{Normality (N)} = \frac{\text{Number of gram equivalents of solute (g eq.)}}{\text{Volume of solution (L)}}$$

$$\text{Normality (N)} = \frac{\text{Mass of solute (g)}}{\text{Equivalent mass (g)} \times \text{Volume of solution (L)}}$$

(b) Molarity (M)

The number of moles of solute present in one litre solution is called its molarity(M).

$$\text{Molarity} = \frac{\text{Number of moles of solute}}{\text{Volume of solution (L)}} = \frac{n}{V_{(L)}}$$

(c) Formality (F)

It is the number of gram formula mass units of solute present per litre of solution. Formality is generally used for solutions of ionic compounds.

$$\text{Formality} = \frac{\text{Mass of solute (g)}}{\text{Formula mass of solute (g)} \times \text{Volume of solution (L)}}$$

(d) Molality (m)

The number of moles of solute present in 1000 gram of the solvent is called as molality of the solution.

$$\text{Molality of a solution} = \frac{\text{Number of moles of solute}}{\text{weight of solvent (kg)}} = \frac{\text{Number of moles of solute} \times 1000}{\text{weight of solvent (g)}}$$

(e) Strength of a Solution (S)

The mass of solute in g dissolved in 1L solution is known as its strength in g L^{-1}.

$$S = \frac{\text{Mass of solute (g)}}{\text{Volume of solution (L)}}$$

$S(gL^{-1})$ = Molarity of solution × Molar mass of solute

$S(gL^{-1})$ = Normality of solution × Equivalent mass of solute

Illustration 1:

If 0.4 g of NaOH is present in 40 mL of solution. What is the molarity and normality of solution [Molecular mass of NaOH = 40]

Solution:

We know that

$$\text{Molarity} = \frac{\text{Mass of solute} \times 1000}{\text{Molar Mass of solute} \times \text{Volume of solution (mL)}}$$

$$M = \frac{0.4}{40 \times 40} \times 1000 = 0.25\ M$$

$$\text{Normality} = \frac{\text{Mass of solute}}{\text{Equivalent mass of solute} \times \text{volume of solution(mL)}} \times 1000$$

Equivalent mass of NaOH = 40

$$N = \frac{0.4}{40 \times 40} \times 1000 = 0.25N$$

Illustration 2:

The normality of 1.5M H_3PO_4 is –

Solution:

Basicity of H_3PO_4 is 3

We know that $N = M \times n \Rightarrow$ Normality = 1.5 × 3 = 4.5 N

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Illustration 3:

Find out the mass of H_2SO_4 in 150 mL, $\frac{N}{7}$ H_2SO_4 solution

Solution:

$$N = \frac{\text{Mass in gram}}{\text{Equivalent mass} \times \text{Volume(L)}}$$

Mass in gram = Equivalent mass × N × Volume (L) = $49 \times \frac{1}{7} \times \frac{150}{1000} = \frac{21}{20} = 1.05g$

Illustration 4:

A 100 cm^3 solution is prepared by dissolving 2g of NaOH in water. Calculate the normality of the solution.

Solution:

$2g\ NaOH = \frac{2}{40}$ g eq; $\quad N = \frac{\frac{1}{20}}{100} \times 1000 = \frac{1}{2}$

Normality of solution = $\frac{N}{2}$

Concentration in terms of percentage

(i) Percent By Mass (w/W)

Mass of solute (in g) present in 100 g of solution (g) is called mass percent of the solute.

Where 'w' gram of solute is dissolved in W gram of solvent.

$$\text{Mass percent} = \frac{\text{Mass of solute}(g) \times 100}{\text{Mass of solution}(g)} = \frac{w \times 100}{w + W}$$

Mass percent is independent of temperature.

(ii) Percent By Volume (v/V)

The volume of solute in mL present in 100 mL of solution is called volume percent.

$$\text{Volume percent} = \frac{\text{Volume of solute} \times 100}{\text{Volume of solution}}$$

(iii) Percent by strength /percentage mass by volume $\left(\frac{w}{V}\right)$**:** Mass of solute (in g) present in 100 mL solution is called percent mass by volume.

$$\% \left(\frac{w}{V}\right) = \frac{\text{mass of solute } (g)}{\text{volume of solution } (mL)} \times 100$$

Parts Per Million (ppm)

This method is used for expressing the concentration of very dilute solutions such as hardness of water, pollutants in air etc.

$$\text{ppm of substance (by mass)} = \frac{\text{Mass of solute}(g) \times 10^6}{\text{Mass of solution}(g)}$$

$$\text{ppm (by volume)} = \frac{\text{Volume of solute(mL)} \times 10^6}{\text{Volume of solution(mL)}}$$

$$\text{ppm}\left(\text{by}\ \frac{w}{V}\right) = \frac{\text{mass of solute } (g)}{\text{volume of solution } (mL)} \times 10^6$$

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Mole Fraction

The ratio of the number of moles of one component to the total number of moles of all the components present in the mixture, is called the mole fraction of that component.

$$\text{Mole fraction of solute, } X_B = \frac{\text{moles of solute}(n)}{\text{moles of solute }(n)+\text{moles of solvent}(N)}$$

$$\text{Mole fraction of solvent, } X_A = \frac{\text{moles of solvent}(N)}{\text{moles of solute }(n)+\text{moles of solvent}(N)}$$

$$\boxed{X_A + X_B = 1}$$

(i) Relation Between Molarity and Normality

S = Molarity × Molar mass of solute and S = Normality × Equivalent mass of solute.

So we can write

Molarity × Molar mass of solute = Normality × Equivalent mass of solute.

$$\text{Normality} = \frac{\text{Molarity} \times \text{Molar mass of solute}}{\text{Equivalent mass of solute}}$$

$$= \frac{\text{Molarity} \times \text{Molar mass of solute}}{(\text{Molar mass of solute/valency factor})}$$

Normality = Molarity × Valency factor

N = M × n factor

(ii) Relation Between Molality (m) and Mole fraction (X_B)

$$\frac{x_B}{x_A} = \frac{n_B}{N_A} = \frac{n_B \times M_A \times 1000}{W_A \times 1000}$$

$$\Rightarrow \frac{x_B}{x_A} = \frac{\text{molality} \times M_A}{1000}$$

$$\frac{x_B}{1-x_B} = \frac{\text{molality} \times M_A}{1000}$$: if x_B <<< 1 for very dilute solution $x_B = \frac{\text{molality} \times M_A}{1000}$

Illustration 5:

Find out the molarity of 93% (w/W) H_2SO_4 (density = 1.84 g/mL).

Solution:

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of solution(L)}} = \frac{\text{Mass in gram} \times \text{Density} \times 1000}{\text{Molar mass} \times \text{mass of solution (g)}}$$

$$= \frac{93 \times 1.84 \times 1000}{98 \times 100} = 17.46 \text{ M}$$

Illustration 6:

Find the percentage by mass and mass fraction of aspirin in the solution prepared by dissolving 3.65 g of aspirin in 25.08 g of water.

Solution:

Mass of solution = 3.65 + 25.08 = 28.73 g

$$\text{Mass fraction of aspirin} = \frac{3.65}{28.73} = 0.127$$

Mass percent of aspirin = 0.127 × 100 = 12.7%

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Illustration 7:

A solution was prepared by adding 125 cm^3 of isopropyl alcohol to water until the volume of the solution was 175 cm^3. Find the volume fraction and volume percent of isopropyl alcohol in the solution.

Solution:

Volume of solute = 125 cm^3

Volume of solution = 175 cm^3

$\therefore$ Volume fraction $= \frac{125}{175} = 0.714$

Volume percent $= \frac{125}{175} \times 100 = 71.4\%$

BEGINNER'S BOX-1

1. What is the normality of 2M H_3PO_2 solution?

(1) 0.5 N (2) 1.0N (3) 2.0 N (4) 3.0 N

2. 23 g ethanol is dissolved in 36 g water. Find mole fraction of ethanol?

(1) 2 (2) 0.5 (3) 0.2 (4) 0.8

3. How many gram of HNO_3 is required to prepare 400 mL solution of 0.2 M HNO_3?

(1) 5.04 g (2) 5040 g (3) 25.2 g (4) 2.52 g

4. Calculate normality of 2.1% (w/V) H_2SO_4 solution?

(1) 2.14 N (2) 4.28 N (3) 0.428 N (4) 0.214 N

5. What is the molarity of 1N H_2SO_4 solution?

(1) 1 M (2) 2M (3) 0.5 M (4) 3M

6. 20.6 g NaBr is dissolved in 500 mL solution what is the molarity of resulting solution?

(1) 0.6 (2) 0.4 (3) 1 (4) None

7. Calculate molality of the solution obtained by dissolving 11.7 g NaCl in 500 g water

(1) 0.1 m (2) 0.3 m (3) 0.2m (4) 0.4m

8. Density of 2.03 M aqueous solution of acetic acid is 1.017 g mL^{-1} molecular mass of acetic acid is 60. Calculate the molality of solution?

(1) 2.27 (2) 1.27 (3) 3.27 (4) 4.27

9. A molar solution is one that contains one mole of solute in

(1) 1000 g of the solvent (2) One litre of the solution

(3) 1000 g of the solution (4) 22.4 litres of the solution

10. Calculate the mole percentage of CH_3OH and H_2O respectively in 60% (by mass) aqueous solution of CH_3OH

(1) 45.8, 54.2 (2) 54.2, 45.8 (3) 50, 50 (4) 60, 40

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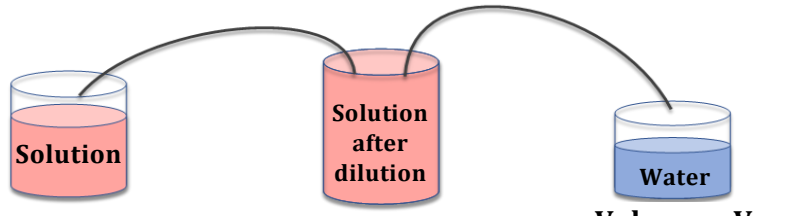
Concept of Dilution

During dilution, solvent is added into solution and moles, gram equivalents, mass of solute remains same



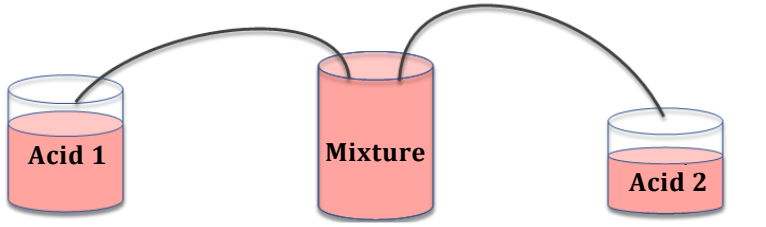
Moles = M_1V_1
g.eq. = N_1V_1

Moles = M_2V_2
g.eq. = N_2V_2
$V_2 = V_1+V_{H_2O}$

$$N_1V_1 = N_2V_2$$
$$M_1V_1 = M_2V_2$$

Concept of Mixing

Case-I



$geq_1 = N_1V_1$

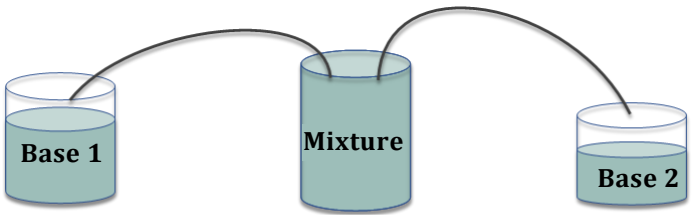
N, V
$NV = N_1V_1 + N_2V_2$
$V = V_1 + V_2$

$geq_2 = N_2V_2$

Normality of $[H^+]$ in Resultant Solution, $[H^+] = \frac{N_1V_1 + N_2V_2}{V_1 + V_2}$

where,
N_1 = Normality of acid 1 solution
N_2 = Normality of acid 2 solution
V_1 = Volume of acid 1 solution
V_2 = Volume of acid 2 solution

Case-II



N_1V_1

N, V
$NV = N_1V_1 + N_2V_2$
$V = V_1 + V_2$

N_2V_2

Normality of $[OH^-]$ in Resultant Solution, $[OH^-] = \frac{N_1V_1 + N_2V_2}{V_1 + V_2}$

where,
N_1 = Normality of base 1 solution
N_2 = Normality of base 2 solution
V_1 = Volume of base 1 solution
V_2 = Volume of base 2 solution

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Illustration 8:

1 litre of 1 N H_2SO_4 solution is diluted by adding 5 litre of water, the normality of that solution is

(1) 0.2 N (2) 5 N (3) 10 N (4) 0.33 N

Solution:

$N_1V_1 = N_2V_2$

$1 \times 1 = N_2 \times 6$

$N_2 = \frac{1}{6} = 0.33$

Illustration 9:

Two solutions of a substance (non-electrolyte) are mixed in the following manner : 480 ml of 1.5M first solution + 520 mL of 1.2M second solution. What is the molarity of the final mixture?

(1) 1.20 M (2) 1.50 M (3) 1.344 M (4) 2.70 M

Solution:

$M_1V_1 + M_2V_2 = M_3V_3$;

$1.5 \times 480 + 1.2 \times 520 = M \times 1000$

$M = \frac{720+624}{1000} = 1.344$ M.

Volume strength of H_2O_2 solution:

Volume of O_2 (L) at NTP/STP produced by decomposition of unit volume solution of H_2O_2 is called its volume strength.

Relationship between volume strength of H_2O_2 and Molarity / Normality / (g/L) / % (w/V)

Let volume strength of H_2O_2 solution be 'X V', it means 1L solution of H_2O_2 can produce X L of O_2 at NTP.

$2H_2O_2 \rightarrow 2H_2O + O_2(g)$

2mol 1mol

$\therefore$ 1 mol O_2 can be produced by = 2 mol H_2O_2 solution

$\therefore$ $\frac{X}{22.4}$ mol of O_2 can be produced by = $\frac{2X}{22.4}$ mol H_2O_2 solution

$= \frac{X}{11.2}$ mol of H_2O_2 solution

(a) Molarity = $\frac{\text{number of moles of solute}}{\text{volume of solution(L)}} = \frac{2X}{22.4} = \frac{X}{11.2}$

Hence, $M = \frac{X}{11.2}$

(b) Normality = molarity × valence factor = $\frac{X}{11.2} \times 2 = \frac{X}{5.6}$

Hence, $N = \frac{X}{5.6}$

(c) Strength (g/L): S = N × E

Hence, $S = \frac{X}{5.6} \times 17 gL^{-1}$

(d) $\%\left(\frac{w}{V}\right) = \frac{X}{5.6} \times \frac{17}{10}$

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Golden Key Points

- If the density of solution is approximately 1g/cc then its Molality > Molarity
- ppm unit is used to represent concentration of very dilute solutions like pollutants in environment and salts present in sea water.
- Those concentration terms which involve volume of solution are temperature dependent.
- Molarity, normality, formality, % by volume, % w/V are temperature dependent.
- Molality, % w/W, mole fraction are temperature independent.

Illustration 10:

Calculate volume strength of H_2O_2 in 5L solution which yields 100 L of O_2 at NTP.

Solution:

5L H_2O_2 gives = 100 L O_2

1L H_2O_2 gives = 20 L O_2

i.e. 20 V H_2O_2 solution

Illustration 11:

Calculate the molarity, normality & strength in "20V H_2O_2" solution.

Solution:

$$\text{Molarity} = \frac{X}{11.2} = \frac{20}{11.2} = 1.78 \text{ M}$$

Normality = molarity × vf = 1.78 × 2 = 3.56 N

$$\text{Strength} = \frac{X}{5.6} \times 17 = \frac{20}{5.6} \times 17 = 60.71 \text{ g/L}$$

Illustration 12:

Calculate the molarity of 20mL of 10V H_2O_2 Solution

Solution:

$$\text{Molarity} = \frac{X}{11.2} = \frac{10}{11.2} = 0.89 \text{ M}$$

Vapour Pressure

At a constant temperature, the pressure exerted by the vapours of a liquid on its surface when they (liquid and its vapours) are in equilibrium, is known as vapour pressure.

Factor affecting Vapour Pressure

- **(a) Nature of Liquid**
- **(b) Temperature**

Raoult's Law

(a) For liquid-liquid system: For a solution of volatile liquids the partial vapour pressure of any component at constant temperature is equal to vapour pressure of pure component multiplied by mole fraction of that component in the solution.

	Liquid (B)	Liquid (A)
Vapour pressure in pure state	P_B^0	P_A^0
Partial Vapour pressure	P_B	P_A
Mole fraction in solution	X_B	X_A
Moles	n moles	N moles
Mass	W(g)	W(g)
Molar mass	m	M

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$P_A \propto X_A$ so $P_A = P_A^0 X_A$ ...(i)

$P_B \propto X_B$ so $P_B = P_B^0 X_B$ ...(ii)

At constant temperature, partial vapour pressure of a component is directly proportional to the mole fraction of component in solution.

According to Dalton's law given below:

- $P_{total} = P_A + P_B + ...$

$P_S = X_A P_A^0 + X_B P_B^0$; $X_A + X_B = 1$

$P_S = (1 - X_B) P_A^0 + X_B P_B^0$

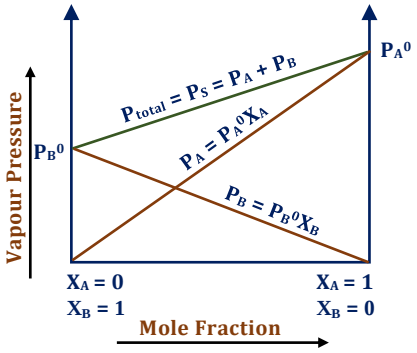
$P_S = P_A^0 - X_B P_A^0 + X_B P_B^0$

$P_S = P_A^0 + X_B(P_B^0 - P_A^0)$

$$\underset{y}{P_S} = \underset{c}{P_A^0} + \underset{x}{X_B}\left(\underset{m}{P_B^0} - P_A^0\right)$$

Slope cab be positive or negative

When $P_B^0 > P_A^0$ when $P_A^0 > P_B^0$



Dalton's Law

Partial pressure of gas = mole fraction × total pressure of gas

$P_A = Y_A P_T$

$P_B = Y_B P_T$

$P_A + P_B = P_T$

$X_A P_A^0 = Y_A P_T$ Y_A and Y_B gives mole fraction in vapour phase

$X_B P_B^0 = Y_B P_T$ X_A and X_B gives mole fraction in liquid phase.

Illustration 13:

Methanol and ethanol form an ideal solution. Solution is prepared by mixing 32 g of CH_3OH and 23 g of C_2H_5OH at 300K. At 300K $P^0_{methanol}$ = 90 mm of Hg and $P^0_{ethanol}$ = 51 mm of Hg.

Calculate partial vapour pressure of its constituents and total vapour pressure of solution.

Solution:

$n_{CH_3OH} = \frac{32}{32} = 1$; $n_{C_2H_5OH} = \frac{23}{46} = 0.5$

$X_{CH_3OH} = \frac{1}{1.5} = \frac{2}{3}$; $X_{C_2H_5OH} = \frac{0.5}{1.5} = \frac{1}{3}$

$P_{CH_3OH} = P^0_{CH_3OH} . X_{CH_3OH} = 90 \times \frac{2}{3}$

P_{CH_3OH} = 60 mm of Hg

$P_{C_2H_5OH} = P^0_{C_2H_5OH} . X_{C_2H_5OH} = 51 \times \frac{1}{3}$

$P_{C_2H_5OH}$ = 17 mm of Hg

$P_S = P_{CH_3OH} + P_{C_2H_5OH}$

P_S = 77mm of Hg

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Illustration 14:

A solution has two liquids A & B and vapour pressures of A and B in pure state are P_A^o = 80 torr, P_B^o = 120 torr. Find out the mole fraction of A in vapour phase if initially, equal moles of A & B are taken.

Solution:

$$y_A = \frac{P_A^o x_A}{P_A^o x_A + P_B^o x_B}$$

$n_A = 1 \quad n_B = 1$

$x_A = 0.5 x_B = 0.5$

$$y_A = \frac{80\times0.5}{80\times0.5+120\times0.5} = \frac{40}{40+60} = \frac{40}{100} = 0.4$$

Illustration 15:

Two liquids A & B are mixed to form an ideal solution. The total vapour pressure of solution is. 235 – 135 x Find the value of P_A^o & P_B^o, If x is the mole fraction of B in solution.

Solution:

$P_T = 235 - 135\, x_B$

$x_B \to 0 \qquad P_T \to P_A^o$

$$\boxed{P_A^o = 235}$$

$X_B \to 1 \qquad P_T \to P_B^o$

$P_B^o = 235 - 135$

$$\boxed{P_B^o = 100}$$

Illustration 16:

Ratio of vapour pressures of A & B in pure state is 1 : 2 and ratio of moles of A and B is also 1 : 2, then find out mole fraction of A in vapour phase.

Solution:

$$y_A = \frac{P_A^o x_A}{P_A^o x_A + P_B^o x_B} \qquad \left[X_A = \frac{1}{1+2} = \frac{1}{3},\ X_B = \frac{2}{3}\right]$$

$$= \frac{1\times\frac{1}{3}}{1\times\frac{1}{3}+2\times\frac{2}{3}} = \frac{\frac{1}{3}}{\frac{1}{3}+\frac{4}{3}} = \frac{\frac{1}{3}}{\frac{5}{3}} = \frac{1}{5} = 0.2$$

(b) For solid - liquid system: non-volatile solute (B) and volatile solvent (A)

$P_B^0 = 0$

$P_S = X_A P_A^0 + X_B P_B^0$

$$P_S = X_A P_A^{\ 0} = \frac{N}{n+N} P_A^0 \qquad \text{...(i)}$$

For solution of non-volatile solute: At constant temperature vapour pressure of solution containing non-volatile solute is proportional to mole fraction of solvent.

$\therefore \quad P_S \propto \frac{N}{n+N}$; $X_A + X_B = 1$

$P_S = (1 - X_B)\, P^0_A$; $P_S = P^0_A - X_B P^0_A$

$$X_B P^0_A = P^0_A - P_S \quad \Rightarrow \quad \frac{P_A^0 - P_S}{P_A^0} = X_B = \frac{n}{n+N} \qquad \text{...(ii)}$$

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- When a non-volatile solute is added to a volatile liquid its vapour pressure decreases because less number of solvent particles present in solution at surface decreases (as compared to pure solvent)

$\therefore$ less vapour is formed and vapour pressure of solution decreases

$P_A^0 - P_S = \Delta P$ (lowering of vapour pressure)

$\frac{P_A^0 - P_S}{P_A^0}$ = relative lowering of vapour pressure.

$$\frac{P_A^0}{P_A^0 - P_S} = \frac{n+N}{n} \qquad \Rightarrow \frac{P_A^0}{P_A^0 - P_S} = 1 + \frac{N}{n}$$

$$\Rightarrow \frac{P_A^0 - P_A^0 + P_S}{P_A^0 - P_S} = \frac{N}{n} \qquad \Rightarrow \frac{P_S}{P_A^0 - P_S} = \frac{N}{n}$$

$$\Rightarrow \frac{P_A^0 - P_S}{P_S} = \frac{n}{N} \qquad \text{...(iii)}$$

$$\Rightarrow \Delta P \propto \frac{n}{N}$$

Ex. The vapour pressure of pure liquid A is 40 torr at 310 K. The vapour pressure of this liquid in solution with solid B is 32 torr. Calculate X_A in solution.

Sol. $32 = X_A \times 40$

$X_A = 0.8$

Colligative Properties of dilute solutions (CP)

Those physical properties of a solution which depends upon the relative number of particles of solute and do not depend on nature of solute particles are called as colligative properties.

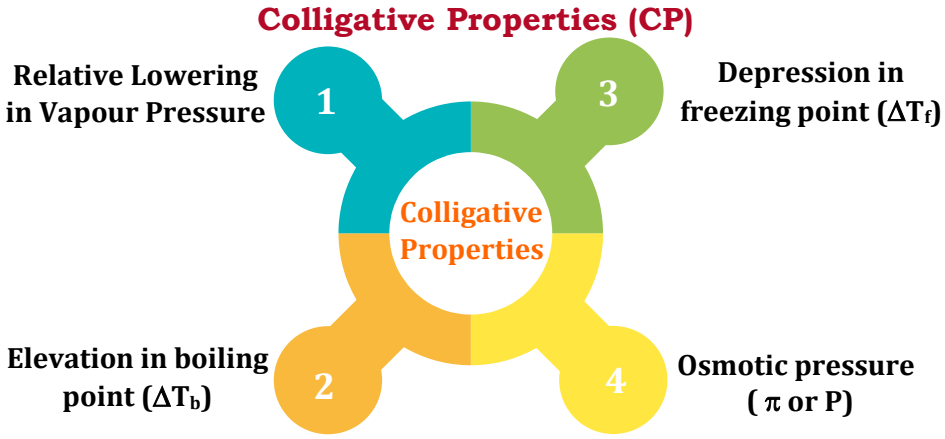
CP $\propto$ Number of solute particles

$\propto$ Number of molecules (in the solution of non electrolyte)

$\propto$ Number of ions (in the solution of electrolytes)

$\propto$ Number of moles of solute

$\propto$ Mole fraction of solute



(a) Relative Lowering in Vapour Pressure

- When a nonvolatile solute is dissolved in a pure solvent, the vapour pressure of the solvent is lowered i.e. the vapour pressure of a solution is always lower than that of pure solvent, because the escaping tendency of solvent molecules decreases (due to lesser solvent molecules per unit surface area).

If at a certain temperature, P° is the vapour pressure of pure solvent and Ps is the vapour pressure of solution, then,

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According to Raoult's law:

Relative lowering in vapour pressure $= \frac{P_A^0 - P_S}{P_A^0} = \frac{n_B}{N_A + n_B}$

For a dilute solution $n_B << n_A$ $\therefore \frac{P_A^0 - P_S}{P_A^0} \approx \frac{n_B}{N_A}$ so $\Delta P \propto \frac{n_B}{N_A}$

- Relative lowering depends upon relative number of solute particles. Therefore, it is called as a colligative property.

Illustration 17:

At 100°C, vapour pressure of aqueous solution of glucose is 750 mm of Hg. Find the mole fraction of the solute.

Solution:

At 100°C, P^o for H_2O = 760 mm Hg

P_S = 750 mm Hg

$\frac{P^o - P_S}{P^o} = X_B$

$\frac{760-750}{760} = x_B$ $\boxed{x_B = \frac{1}{76}}$

Illustration 18:

Find the mass of urea which should be dissolved in 360 g water so that vapour pressure of solution is decreased upto 6/7 times the vapour pressure of pure water.

Solution:

Mass of solvent = 360 g, $P_S = \frac{6}{7}P^o$

$\frac{P^o - P_S}{P_S} = \frac{n}{N}$

$\frac{P^o - \frac{6}{7}P^o}{\frac{6}{7}P^o} = \frac{\frac{w}{60}}{\frac{360}{18}}$

w = 200 g

Illustration 19:

60% by mass of urea is present in an aqueous solution at 100°C. Find the value of lowering in vapour pressure ?

Solution:

For water, at 100° C, P^o = 760 mm Hg.

$\frac{P^o - P_S}{P^o} = \frac{n}{n+N}$

60% by mass urea

60 gm urea in 100 gm solution

$n = \frac{60}{60} = 1 \text{ mol}$, $N = \frac{100-60}{18} = \frac{40}{18} = 2.22$

$\frac{P^o - P_S}{760} = \frac{1}{1+2.22}$

$P^o - P_S$ (lowering in vapour pressure) $= \frac{760}{3.22} = 236.02$ mm Hg

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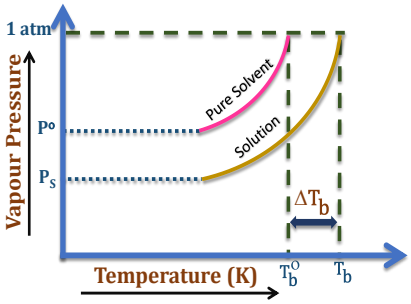
(b) Elevation in Boiling Point



T_b = Boiling point of solution
T^0_b = Boiling point of solvent
The vapour pressure curve for solution lies below the curve for pure water.
The diagram shows that ΔT_b denotes
The elevation in boiling point of a Solvent in solution

- The boiling point of a liquid is that temperature at which its vapour pressure becomes equal to the atmospheric pressure.
- When a non-volatile solute is dissolved in a pure solvent, its vapour pressure is decreased and boiling point increases. The difference of boiling points of the solution and pure solvent is called elevation in boiling point. (ΔT_b)
- If T^0_b is the boiling point of pure solvent and T_b is the boiling point of the solution then, $T_b > T^0_b$ and the elevation in boiling point $\Delta T_b = T_b - T^0_b$
- The elevation in boiling point (ΔT_b) is directly proportional to lowering of vapour pressure of the solution i.e.

$\Delta T_b \propto (P^o - P_s)$ from graph and $\Delta T_b \propto \Delta P \propto \frac{n_B}{N_A}$

$\therefore \quad \Delta T_b \propto \frac{n_B}{N_A} = \frac{w_B M_A}{m_B W_A}$ (for a solvent P^0 & M_A = constant)

$\therefore \quad \Delta T_b \propto \frac{w_B}{m_B W_A}$ or $\Delta T_b = \frac{K w_B}{m_B W_A}$

where K = elevation constant

if $\frac{w_B}{m_B}$ = 1 mole and W_A = 1 g

then ΔT_b = K (Elevation constant or molecular elevation constant)

if $\frac{w_B}{m_B}$ = 1 and W_A = 1000 gram; Then $\Delta T_b = K_b$ (molal elevation constant)

$\therefore \quad \frac{K}{1000} = K_b$ (molal elevation constant or Ebullioscopic constant)

$\Delta T_b = \frac{K_b \times w_B \times 1000}{m_B \times W_A}$; $\Delta T_b = \frac{w_B}{m_B} \times \frac{1000}{W_A} \times K_b$

$\therefore \quad \Delta T_b = \text{molality} \times K_b \qquad \therefore \quad \Delta T_b \propto \text{molality}$

hence elevation in boiling point (ΔTb) is a colligative property.

- K_b depends only on nature of solvent which can be explained by thermodynamic relation.

$K_b = \frac{RT_b^{0^2}}{1000 L_v} = \frac{M_w RT_b^{0^2}}{1000 \Delta H_{vap}}$

Where T_b^0 = Boiling point of solvent.

M_w = Molar mass of solvent.

ΔH_{vap} = Enthalpy of vapoursation per mole of solvent

L_v = Latent heat of vapourisation per gram of solvent

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The molal elevation constant for some common solvents are given in the following table

Solvent	B.P. (°C)	Molal elevation constant (K_b)
Water	100.0	0.52
Acetone	56.0	1.70
Chloroform	61.2	3.63
Carbon tetra chloride	76.8	5.03
Benzene	80.0	2.53
Ethyl alcohol	78.4	1.20

Illustration 20:

30 g of urea is present in 100 g of water. Find out the boiling point of solution in °C.

Solution:

$T_b - T_b^o = K_b \times m$

$T_b - 100 = 0.52 \times \frac{30 \times 1000}{60 \times 100}$

$T_b = 102.65^oC$

Illustration 21:

0.86 g of solute (molecular weight = 152) is dissolved in 25 g of acetone. Find the boiling point of solution if boiling point of acetone is 56.2 °C and the value of K_b for acetone per 100 g is 17.

Solution:

$K_b = 17$ per 100 g $= 17 \times \frac{100}{1000} = 1.7$ K. Kg mol^{-1}

$T_b - T_b^o = K_b \times m$

$T_b - 56.2 = 1.7 \times \frac{0.86 \times 1000}{152 \times 25}$

$\Rightarrow \quad T_b = 56.58^oC$

Illustration 22:

The vapour pressure of aqueous solution of sucrose is 732 mm of Hg. Find the b.p. of the solution, if the vapour pressure of pure H_2O is 760 mm of Hg. (K_b of water = 0.52 kg K mol^{-1})

Solution:

$\frac{P_A^o - P_S}{P_A^o} = X_B \Rightarrow \frac{760 - 732}{760} = X_B$

$X_B = 0.036$

$m = \frac{1000 \times X_B}{X_A \times (M_w)_A} = \frac{1000 \times 0.036}{(1 - 0.036) \times 18} = 2.07$

$\Delta T_b = T_b - T_b^o = K_b \times m$

$T_b - 100 = 0.52 \times 2.07$

$T_b = 101.07$ °C

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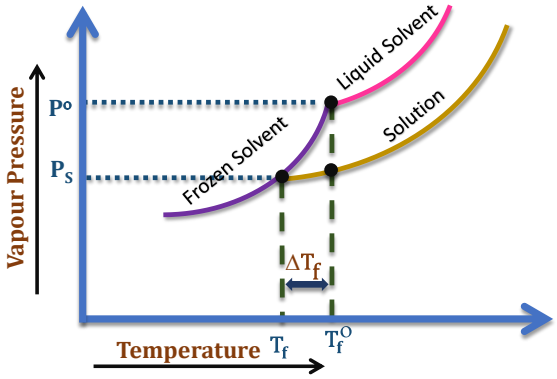
(c) Depression in Freezing Point



- The freezing point of a liquid is that temperature at which the liquid and its solid state exist in equilibrium with each other.
- It may be defined as the temperature at which the liquid and solid states of a substance have the same vapour pressure.
- When a non-volatile solute is dissolved in a pure solvent the vapour pressure of the solvent is lowered.
- If T_f^0 is the freezing point of pure solvent and T_f is the freezing point of its solution then, $T_f < T_f^0$
- The difference in the freezing point of pure solvent and solution is called depression in freezing point (ΔT_f)

  $\Delta T_f = T_f^0 - T_f$; the depression in freezing point is directly proportional to lowering in vapour pressure (ΔP)

  $$\Delta T_f \propto \Delta P \propto \frac{n_B}{N_A} ;\ \Delta T_f \propto \frac{n_B}{N_A} \text{ so } \quad \Delta T_f = K_f \times \text{molality}$$

  K_f = molal depression constant or Cryoscopic constant.
- K_f depends only on nature of solvent which can be explained by the thermodynamic relation,

  $$K_f = \frac{RT_f^{02}}{1000L_f} = \frac{RT_f^{02}M_w}{1000\Delta H_f}$$

  Where T_f^0 = Freezing point of solvent

  M = Molar mass of solvent

  ΔH_f = Enthalpy of fusion per mole of solvent

  L_f = latent heat of fusion per gram of solvent

The molal depression constant for some common solvents are given in the following table

Solvent	F.P.(°C)	Molal depression constant (K_f)
Water	0.0	1.86
Ethyl alcohol	–114.6	1.99
Chloroform	–63.5	4.79
Carbon tetra chloride	–22.8	31.80
Benzene	5.5	5.12
Camphor	179.0	39.70

Illustration 23:

How much gram of glycol is dissolved in 5L H_2O so that freezing point of solution becomes –6°C? (K_f of water = 1.86 Kg K mol^{-1})

Solution:

$\Delta T_f = T_f^o - T_f = K_f \times m$

$$\text{glycol} = \underset{\text{OH}}{\overset{|}{\text{CH}_2}} - \underset{\text{OH}}{\overset{|}{\text{CH}_2}}$$

$[d_{H_2O} = 1g/mL \equiv 1Kg/L]$, so $5L \equiv 5$ Kg

$$0 - (-6) = 1.86 \times \frac{w_B}{62 \times 5}$$

$w_B = 1000$ g

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Illustration 24:

The freezing point of an aqueous solution is –1.5°C. Find the boiling point of the solution.

Solution:

$T_f^o - T_f = K_f \times m,\ T_b - T_b^o = K_b \times m$

$0 - T_f = K_f \times m$ ...(1)

For H_2O $\begin{bmatrix} T_f^o = 0^o C \\ T_b^o = 100^o C \end{bmatrix}$

$T_b - 100 = K_b \times m$ ...(2)

$\frac{eq.(1)}{eq.(2)} \Rightarrow \frac{0-(-1.5)}{T_b - 100} = \frac{1.86}{0.52}$

$\frac{1.5 \times 0.52}{1.86} = T_b - 100$

$T_b = 100.41\ ^oC$

Illustration 25:

How much gram of sucrose is dissolved in 100 g of water so that difference between freezing point & boiling point of solution becomes 105°C? [Given K_b (H_2O) = 0.52 kg K mol^{-1}, K_f(H_2O) = 1.86 kg K mol^{-1}]

Solution:

$T_b - T_b^o = K_b \times m$ ...(1)

$T_f^o - T_f = K_f \times m$ ...(2)

on addition eq. (1) & (2)

$(T_b - T_b^o) + (T_f^o - T_f) = K_b \times m + K_f \times m$

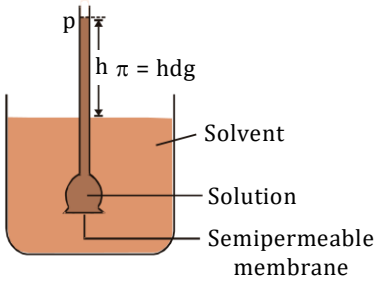
$T_b - 100 + 0 - T_f = m[0.52 + 1.86]$

$105 - 100 = \frac{w_B \times 1000}{342 \times 100} \times 2.38$

$w_B = 71.84$ g

(d) Osmosis and Osmotic Pressure

Osmosis: Osmosis is defined as the spontaneous net flow of solvent molecules through semipermeable membrane from a solvent to a solution or from a dilute solution to a concentrated solution.



Level of solution rises in the thistle funnel due to osmosis of solvent

Osmotic Pressure (p or π)

- The external pressure which must be applied on the solution in order to stop the flow of solvent into the solution through semipermeable membrane is equal to osmotic pressure

or

- Hydrostatic pressure developed in a vertical column when solution and solvent are separated by SPM.

Osmotic pressure = hydrostatic pressure; $\pi = hdg$

where h = increase in level in the tube of unit cross section
d = density of solution
g = acceleration due to gravity

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Van't Hoff law for Dilute Solution

According to it Gas equation, PV = nRT is also followed by dilute solution when pressure of gas is replaced by osmotic pressure of solution.

π = osmotic pressure of solution (atm)

V = volume of solution (L)

n = moles of solute

R = (S) Universal gas constant / Solution constant = 0.0821 L atm $mol^{-1}K^{-1}$; 0.083 L bar $mol^{-1}K^{-1}$

$$\pi = \left(\frac{n}{V}\right)RT \qquad \pi = CRT$$

P V = nRT
↓ ↓ ↓
π V = nRT

At constant temperature $\therefore$ π is a colligative property.

- On the basis of osmotic pressure solution can be classified by following ways:

(i) **Isotonic solutions:** Solutions having same osmotic pressure are called isotonic solution.

$\pi_1 = \pi_2$; primary condition

$C_1RT = C_2RT$ (at same temperature)

$C_1 = C_2$ (secondary condition) ; means

$\frac{n_1}{V_1} = \frac{n_2}{V_2}$; such solutions are known as **isotonic**

(ii) $\pi_1 > \pi_2$ or $C_1 > C_2$ then solution 1 is called **hypertonic** and solution 2 is called **hypotonic**

Reverse Osmosis

If external pressure greater than osmotic pressure is applied, the flow of solvent molecules can be made to proceed from solution towards pure solvent, i.e., in reverse direction of the ordinary osmosis. Reverse osmosis is used for the desalination of sea water for getting fresh drinking water.

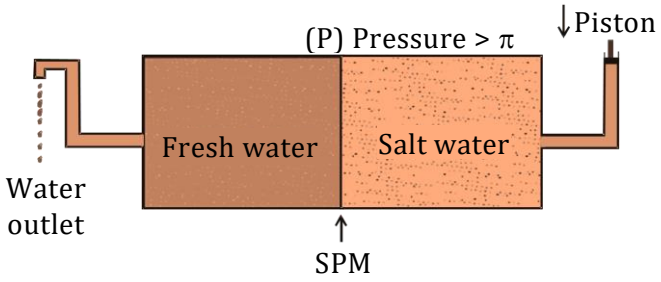

Illustration 26:

0.001 M glucose solution is present in a beaker. Find its osmotic pressure at 27°C temperature.

Solution:

$\pi = CRT = 0.001 \times 0.0821 \times 300 = 0.02463$ atm

Illustration 27:

0.5 g solute is dissolved in 20 mL of solution then the osmotic pressure of solution is 7.6 mm of Hg at 27°C. Find molecular weight of solute.

Solution:

$$\pi = CRT = \frac{w_B}{(M_w)_B \times V(L)} \times RT$$

$$\frac{7.6}{760} = \frac{0.5}{(M_w)_B\left(\frac{20}{1000}\right)} \times 0.0821 \times 300$$

$$\left[1\,atm = 760\,mm\,Hg \quad 1\,mm\,hg = \frac{1}{760}atm\right]$$

$(M_w)_B = 61575$ g mol^{-1}

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Illustration 28:

100 mL of 1.5% urea solution having osmotic pressure 6 atm and 100 mL of 3.42% sucrose solution having osmotic pressure 2.4 atm are mixed with each other. Find the osmotic pressure of resultant solution.

Solution:

$\pi_1V_1 + \pi_2V_2 = \pi_{mix.}V_{mix}$.

$\pi_{mix.} = \frac{6\times100+2.4\times100}{200} \Rightarrow 4.2$ atm

BEGINNER'S BOX-2

1. An example of colligative property :-
(1) Freezing point (2) Boiling point (3) Vapour pressure (4) Osmotic pressure

2. The freezing point order of the solution of glucose is :-
(1) 10% > 3% > 2% > 1% (2) 1% > 2%> 3%> 10%
(3) 1% > 3% > 10% > 2% (4) 10% > 1% > 3% > 2%

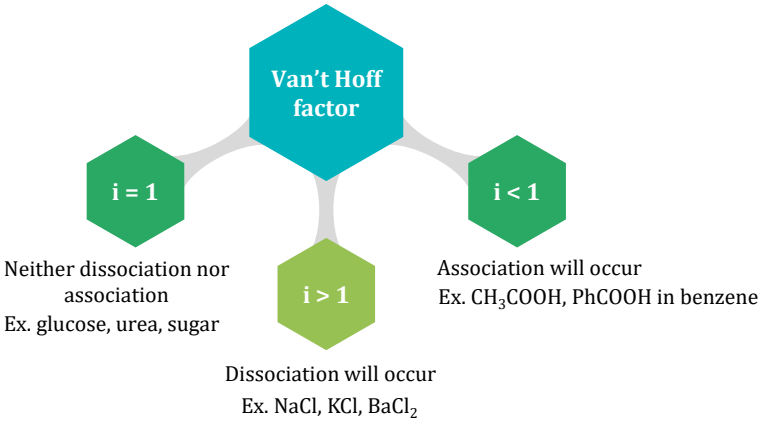
3. In cold countries, ethylene glycol is added to water in the radiators of cars during winters. It result in reducing :-
(1) Viscosity (2) Specific heat (3) Freezing point (4) Boiling point

4. Calculate the molal depression constant of a solvent, which has freezing point 16.6 °C and latent heat of fusion 180.75 Jg^{-1}
(1) 2.68 (2) 3.86 (3) 4.68 (4) 2.86

5. The osmotic pressure of a solution at 0 °C is 4 atm. What will be its osmotic pressure at 546 K under similar condition?
(1) 4 atm (2) 2 atm (3) 8 atm (4) 1 atm

Abnormal colligative properties

- It has been observed that there occurs difference in the observed and calculated molecular masses of solute due to association or dissociation of solute molecules in solution. It results in change in the number of particles in solution.
- **Van't hoff factor (i):** Tells about relationship between normal colligative properties and abnormal colligative properties.
- $i = \frac{\text{number of particles after dissociation or association}}{\text{number of particles before dissociation or association}} = \frac{\text{observed colligative properties}}{\text{calculated colligative properties}} = \frac{\text{calculated molecular mass}}{\text{observed molecular mass}}$



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Case I:

Dissociation of solute: Molecules of electrolytes undergo ionization or dissociation in polar solvents to give two or more particles in solution. This dissociation results in an increase in the total number of particles, and therefore the value of colligative properties of such solutions will be higher than expectation. As the colligative properties are inversely related to molecular weight, so the molecular weight of ionizable solute will be less than the theoretical value.

Number of solute particles in solution increases.

- observed / experimental C.P. > calculated C.P. (normal)
- observed /experimental molecular weight of solute < calculated (normal) molecular weight of solute

$$\therefore \text{ C.P.} \propto \frac{1}{\text{molecular weight of solute}}$$

- Calculation of 'i': Let solute be A_xB_y (electrolyte)

	$A_xB_y \rightarrow$	xA^{y+}	+ yB^{x-} ;	x + y = n (total number of ions)
Initially	1 mol	0	0	
After dissociation	$(1-\alpha)$	$x\alpha$	$y\alpha$	

Total number of solute particles = $1 - \alpha + x\alpha + y\alpha = 1 - \alpha + (x + y)\alpha = (1 - \alpha + n\alpha)$ mol

Observed colligative property is proportional to observed number of solute particles $(1 - \alpha + n\alpha)$

$$i = \frac{\text{number of particles after dissociation}}{\text{number of particles before dissociation}} = \frac{1-\alpha+n\alpha}{1}$$

$i = 1 + (n-1)\alpha$

where α is the degree of dissociation

- For strong electrolytes

If $\alpha = 1$ or 100%

Ex. NaCl $\Rightarrow i = 2$; $\alpha = 100\%$

K_2SO_4 $\Rightarrow i = 3$ $\alpha = 100\%$

Ex. $K_4[Fe(CN)_6] \Rightarrow i = 5$ for $\alpha = 100\%$

For $\alpha = 50\%$ $i = 1 + (n - 1)\alpha$

$i = 3$

Case II:

Association of solute: The formation of a bigger molecule by the union of two, three or more solute molecules is called association. As a result of association, the total number of particles in solution become less than the number of molecules initially put in the solution and hence the colligative properties will have lower value. As the molar mass of solute is inversely proportional to the colligative properties, the molar mass of solute will be greater than theoretical value.

Number of solute particles in solution decreases.

- Observed /experimental C.P. < calculated C.P.
- Observed / experimental molecular weight of solute > normal molecular weight of solute

$$\therefore \text{ C.P.} \propto \frac{1}{\text{Molecular weight of solute}}; \quad i < 1 \text{ for association.}$$

- Calculation of i

	$nA \longrightarrow$	A_n
Initially	1	0
After association	$(1-\alpha)$	$\frac{\alpha}{n}$

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Total number of solute particles = $\left(1-\alpha+\frac{\alpha}{n}\right)$ mol

Observed C.P. $\propto$ observed number of solute particles $\left(1-\alpha+\frac{\alpha}{n}\right)$

Van't hoff factor (i) = $\frac{\text{number of particles after association}}{\text{number of particles before association}}$; $i=\frac{1-\alpha+\frac{\alpha}{n}}{1}$

$i=1-\alpha+\frac{\alpha}{n}$

α = degree of association

n = number of solute particles which are associated.

- If α = 100% or 1 or if α is not specified, then, $\boxed{i=\frac{1}{n}}$

Illustration 29:

The observed and calculated molar mass of $Ba(NO_3)_2$ is 155 g and 260 g respectively. Calculate its degree of ionisation.

Solution:

$i=\frac{\text{calculated molecular mass}}{\text{observed molecular mass}}=\frac{260}{155}=1.67$

$i = 1 + (n - 1)\alpha$

$1.67 = 1 + (3 - 1)\alpha$

$0.67 = 2\alpha$

$\alpha = 0.335$

$\alpha = 33.5\%$

Illustration 30:

$2A \rightarrow A_2$, If degree of association is 80% then, find out its Van't hoff factor.

Solution:

$2A \rightarrow A_2$

$i = 1 - \alpha + \frac{\alpha}{n} = 1 - 0.8 + \frac{0.8}{2} = 0.6$

Illustration 31:

A 0.3 molal aqueous solution of weak acid (HX) is 30% ionised. Calculate the elevation in B.P. of this solution.

Solution:

$i = 1 + (n - 1)\alpha$

$i = 1 + (2 - 1)\ 0.3$

$i = 1 + 0.3 = 1.3$

$\Delta T_b = K_b \times m \times i$

$\Delta T_b = 0.52 \times 0.3 \times 1.3$

$\Delta T_b = 0.2°C$

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Illustration 32:

11 g $Ba(NO_3)_2$ is added to 100 g H_2O, then solution is boiled at 100.46°C. Find out the degree of ionisation of salt (molecular weight $Ba(NO_3)_2$ = 260)

Solution:

$$\Delta T_b = \frac{i \times k_b \times w_B}{M_{w_B} \times w_A} \times 1000$$

$$0.46 = \frac{i \times 0.52 \times 11 \times 1000}{260 \times 100}$$

$i = 2.09$

$i = 1 + (n - 1)\alpha$

$2.09 = 1 - \alpha + 3\alpha$

$2\alpha = 1.09$

$\alpha = 0.545$

Illustration 33:

Which of the following solution of glucose has highest vapour pressure?

(1) 1M (2) 0.1 M

(3) 0.01 M (4) All have same vapour pressure

Solution:

RLVP (C.P.) $\propto$ (i × M)

M ↑ $\Rightarrow$ RLVP ↑ $\Rightarrow$ V.P.↓

Hence, Ans is (3)

Illustration 34:

A 5% solution of anhydrous $CaCl_2$ at 0°C developed 15 atm osmotic pressure. What is the degree of dissociation of $CaCl_2$?

Solution:

5 g. of $CaCl_2$ are present in 100 mL,

so 111 g (M_W of $CaCl_2$) will be present in $\frac{100 \times 111}{5 \times 1000} = 2.22$ L

Now $\pi V = ST$ {$\because n = 1$} or $\pi = \frac{0.082 \times 273}{2.22} = \frac{22.47}{2.22} = 10.09$ atm

We know that Van't Hoff factor = $\frac{\text{observed colligative property}}{\text{Normal colligative property}} = \frac{15}{10.09}$

and $\alpha = \frac{i-1}{n-1}$ or $\alpha = \frac{\frac{15}{10.09} - 1}{3-1} = \frac{4.91}{10.09 \times 2} = 0.2433$ or 24.33%

Illustration 35:

Calculate the osmotic pressure of 20% (wt/Vol.) anhydrous $CaCl_2$ solution at 0°C assuming 100% ionisation.

Solution:

	$CaCl_2$	$\rightarrow$	Ca^{2+}	+	$2Cl^-$
Before dissociation	1		0		0
After dissociation	1 – α		α		2α

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Given, w = 20 g, V = 100 mL, T = 273 K,

Mol wt. of $CaCl_2$ = 111

$$\pi_{Normal} = \frac{w}{mV} \times S \times T = \frac{20 \times 1000 \times 0.0821 \times 273}{111 \times 100} = 40.38 \text{ atm.}$$

Now, $i = \frac{1+2\alpha}{1} = 1+2 = 3 \ (\because \alpha = 1)$

$\pi_{exp} = i \times \pi_{Normal} = 40.38 \times 3 = 121.14$ atm

Illustration 36:

When 0.2 g acetic acid is added to 20 g benzene, then freezing point decreases by 0.45°C. Find out the degree of association. (k_f for benzene = 5.12°Cm^{-1})

Solution:

$$\Delta T_f = \frac{i \times k_f \times w_B}{Mw_B \times w_A} \times 1000$$

$$\Rightarrow 0.45 = \frac{i \times 5.12 \times 0.2}{60 \times 20} \times 1000$$

$$i = 0.527, \quad i = 1 + \left(\frac{1}{n} - 1\right)\alpha$$

$$0.527 = 1 + \left(\frac{1}{2} - 1\right)\alpha$$

$\alpha = 0.946$

BEGINNER'S BOX-3

1. Calculate the percentage degree of dissociation of an electrolyte AB_2(normal molar mass = 164) in H_2O if observed molar mass is 65.6

(1) 50% (2) 25% (3) 75% (4) None

2. Which of the following solution will have highest freezing point

(1) 1M urea (2) 1M Na_2SO_4 (3) 1M NaCl (4) 1M $Al_2(SO_4)_3$

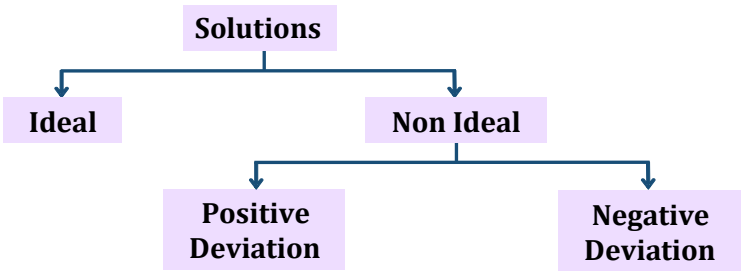
3. A 1.17% solution of NaCl is isotonic with 7.2% solution of glucose calculate the value of i of NaCl

(1) 1 (2) 2 (3) 3 (4) 4

4. Van't hoff factor of Hg_2Cl_2 in its aqueous solution will be (Hg_2Cl_2 is 80% ionized in the solution)

(1) 1.6 (2) 2.6 (3) 3.6 (4) 4.6

Ideal & Non Ideal Solutions, Azeotropic mixtures



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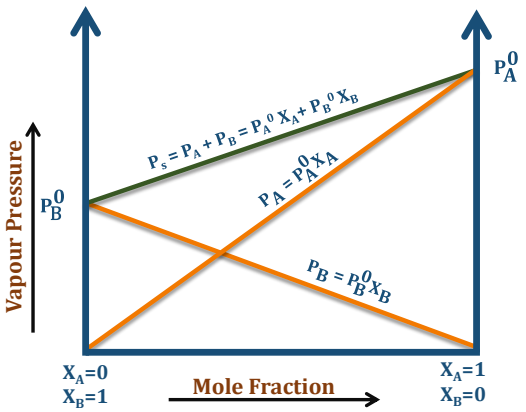
Ideal solutions (mixture of two liquids A and B)



- A solution which obeys Raoult's law at all concentrations and at all temperatures is called an ideal solution.
- For ideal solutions;
  A-A interactions = B-B interactions = A-B interactions.
  An ideal solution possesses the following characteristics:
- Volume change on mixing should be zero.
  $\Delta V_{mix} = 0$, i.e., $(V_{solute} + V_{solvent} = V_{solution})$
- Heat change on mixing should be zero.
  $\Delta H_{mix} = 0$ (Heat is neither absorbed nor evolved)
- There should be no chemical reaction between liquid A and liquid B.
- Ideal solution must obey Raoult's law at all concentrations.
  $P_A = P_A^0 X_A$, $P_B = P_B^0 X_B$
- observed VP = calculated VP
- observed BP = calculated BP
- $\Delta S_{mix} > 0$, $\Delta G < 0$

Example

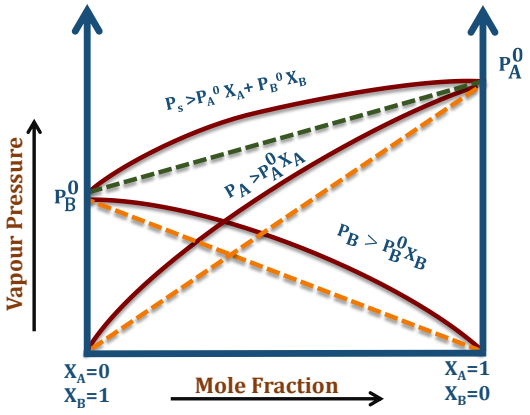
(i) Benzene and toluene (ii) CCl_4 and $SiCl_4$ (iii) n-hexane and n-heptane
(iv) C_2H_5Br and C_2H_5Cl (v) PhCl and PhBr (vi) n-butylchloride and n-butylbromide

Non-ideal Solutions

- For non ideal solutions; A – A interactions or B-B interactions ≠ A – B interactions.
- Those solutions which do not obey Raoult's law are called non-ideal solutions.
- For such solutions ; $P_A \neq P_A^o X_A$; $P_B \neq P_B^o X_B$
- Non ideal solutions are formed when the components differ much in their structures and polarities.
  So $\Delta H_{mixing} \neq 0$ and $\Delta V_{mixing} \neq 0$
- Non ideal solutions show either positive or negative deviations from Raoult's law.

(a) Non ideal solutions having positive deviation from Raoult's law.

- In these solutions A-B interactions are less than A-A and B-B molecular interactions.
  $P_A > P_A^o X_A$, $P_B > P_B^o X_B$



- The total vapour pressure of the solution will be greater than the corresponding vapour pressure than expected in case of an ideal solution of same composition.
  i.e. $P_{total} > (P_A^o X_A + P_B^o X_B)$
- $\Delta H_{mix} > 0$; endothermic dissolution ; heat is absorbed.
- $\Delta V_{mix} > 0$; volume increases after dissolution,
  i.e., $(V_{solute} + V_{solvent} < V_{solution})$.
- 'A' and 'B' escape easily showing higher vapour pressure than the expected value.
  $(B.P.)_{th} > (B.P.)_{exp}$
- $(\Delta S)_{mix}$ = +ve , ΔG = –ve
  Entropy change in mixing is positive.

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Examples:

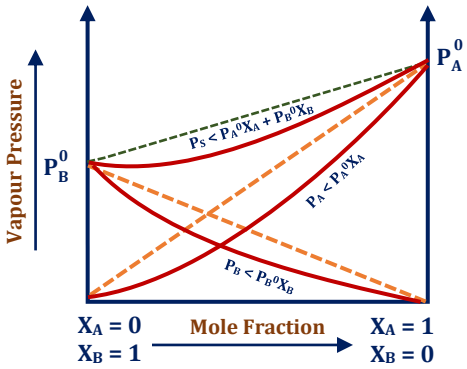
(i) Ethanol and cyclohexane (ii) Ethanol and Water (iii) Ethanol and Acetone
(iv) Methanol and H_2O (v) CCl_4 and Benzene (vi) CCl_4 and Toluene
(vii) CCl_4 and $CHCl_3$ (viii) CCl_4 and Methanol (ix) Benzene and Acetone
(x) CS_2 and Acetone (xi) CS_2 and Acetaldehyde

(b) Non ideal solutions having negative deviation from Raoult's Law

- In these solutions the A-B interactions are stronger than the A-A and B-B molecular interactions.

  $P_A < P_A^o X_A$; $P_B < P_B^o X_B$
- $P_{total} < (P_A^o X_A + P_B^o X_B)$

  Total vapour pressure is less than sum of individual vapour pressure.
- $\Delta H_{mix} < 0$; exothermic dissolution heat is evolved.
- $\Delta V_{mix} < 0$; volume decreases during dissolution, i.e., (V_{solute} + $V_{solvent} > V_{solution}$).
- Escaping tendency of both components 'A' and 'B' is lowered showing lower vapour pressure than expected ideally.



Examples:

(i) $CHCl_3$ and CH_3COCH_3 (ii) $CHCl_3$ and C_6H_6 (iii) $CHCl_3$ and $C_2H_5OC_2H_5$
(iv) $CHCl_3$ and HNO_3 (v) $CHCl_3$ and CH_3COOH (vi) H_2O and HCl
(vii) H_2O and HNO_3 (viii) CH_3COOH and CH_3OH (ix) CH_3COOH and C_5H_5N
(x) CH_3COCH_3 and Aniline

Azeotropic mixtures:

Some liquids on mixing form azeotropes which are binary mixtures having the same composition in liquid and vapour phase and boil at a constant temperature. The liquid and vapour have the same composition and no further separation occurs.

Components forming azeotrope can't be separated by fractional distillation but can be separated by azeotropic distillation.

Solutions showing Positive deviation form minimum boiling azeotrope and solutions showing negative deviation form maximum boiling azeotrope.

There are two types of azeotropes:

(a) Minimum boiling azeotrope
(b) Maximum boiling azeotrope

(a) The solutions which show a large positive deviation from Raoult's law form minimum boiling azeotrope at a specific composition. For example, ethanol-water mixture (obtained by fermentation of sugars) on fractional distillation gives a solution containing approximately 95.57% v/v ethanol.

(b) The solutions that show large negative deviation from Raoult's law form maximum boiling azeotrope at a specific composition. Nitric acid and water is an example of this class of azeotrope. This azeotrope has the approximate composition, 68% nitric acid and 32% water by mass, with a boiling point of 393.5 K.

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Golden Key Points

- ΔS is positive and ΔG is negative for ideal as well as non ideal solutions.
- The vapour phase is richer in more volatile component than the less volatile component. This is called as Konowaloff's rule.

Illustration 37:

1 mole heptane (V.P. = 92 mm of Hg) is mixed with 4 mole octane (V.P. = 31 mm of Hg) to form an ideal solution. Find out the vapour pressure of solution.

Solution:

Total mole = 1 + 4 = 5

Mole fraction of heptane $X_A = 1/5$

Mole fraction of octane $X_B = 4/5$

$P_S = X_A P_A^0 + X_B P_B^0 = \frac{1}{5}\times 92 + \frac{4}{5}\times 31 = 43.2$ mm of Hg.

Illustration 38:

At 88°C, benzene has a vapour pressure of 900 torr and toluene has a vapour pressure of 360 torr. What is the mole fraction of benzene in the mixture with toluene that will be boil at 88°C at 1 atm pressure? (benzene – toluene form an ideal solution).

Solution:

P_S = 760 torr, because solution boils at 88°C

$P_S = P_B^0 X_B + P_T^0 X_T$

$\therefore \quad 760 = 900\,a + 360 - 360\,a$

a = 0.74 where 'a' is mole fraction of $C_6H_6(X_B)$

Illustration 39:

10 mL of liquid A (B.P. = 368 K) and 10 mL of liquid B(B.P. = 415 K) are mixed to obtain 19.92 mL of a constant boiling mixture, then, B.P. of the solution is

(1) < 368 K (2) > 368 K but < 415 K

(3) > 415 K (4) unpredictable

Solution:

According to definition,

Experimental volume is less than theoretical, hence, Negative deviation and azeotrope is maximum boiling.

Hence B.P. of solution > 415 K

Solubility

Maximum amount of solute which can be dissolved in a specified amount of solvent at constant temperature is known as solubility. Solubility is affected by nature of solute and solvent as well as by temperature and pressure.

(a) Solubility of Solid in Liquid

Polar solutes are soluble in polar solvent and non polar solutes are soluble in non polar solvent due to similar intermolecular forces.

When solid solutes are dissolved in solvent, then following equilibrium exists:

Solute + Solvent ⇌ Solution

Solubility of solids is affected by temperature and pressure according to Le-Chatelier's principle. If dissolution is exothermic, then, solubility decreases with increase in temperature and if endothermic, then, solubility increases with increase in temperature.

Solubility of solids is not affected by pressure significantly since solids are highly incompressible.

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(b) Solubility of Gases in Liquid

Certain gases are highly soluble in water like NH_3, HCl etc. and certain gases are less soluble in water like O_2, N_2, He etc. Solubility of gases is affected by pressure and temperature. Increase in pressure increases solubility and increase in temperature decreases solubility. During dissolution of gas pressure of gas decrease and its dissolution is also exothermic in nature.

Henry's Law

It can be stated that at constant temperature the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas present above the surface of liquid or solution.

or

Mole fraction of gas in the solution is proportional to the partial pressure of the gas over the solution.

or

The partial pressure of the gas in vapour phase (P) is proportional to the mole fraction of the gas (X) in the solution. (This is the most common definition)

$P = K_H X$ K_H = Henry's Constant

Henry's Constant is not a universal constant. It depends on nature of gas and temperature. K_H increases with increase in temperature therefore solubility of gas decreases.

Golden Key Points

- Those gases which can react with solvent do not follow Henry's Law. e.g. NH_3 in water.
- Raoult's Law is special case of Henry's Law.

Illustration 40:

Henry's Law Constant for CO_2 in water is 1.67×10^8 P_a at 298K. Calculate the quantity of CO_2 in 1 L of soda water when packed under 2.5 atm CO_2 pressure at 298 K.

Solution:

$P = K_H X_{gas}$

$$X_{gas} = \frac{P}{K_H} = \frac{2.5\times10^5}{1.67\times10^8} = 1.5\times10^{-3}$$

$$\frac{n}{n+N} = X$$

$$\frac{n}{N} = X \because \ n << N \quad \therefore n + N \simeq N$$

$$\frac{n}{55.55} = 1.5 \times 10^{-3} = 8.3 \times 10^{-2} \text{ mol } L^{-1} = 3.65 \text{ g } L^{-1}$$

Illustration 41:

The Henry's law constant for the solubility of nitrogen gas in water at 298 K is 1×10^5 atm. The mole fraction of nitrogen in air is 0.8. Calculate the number of moles of nitrogen from air dissolved in 10 moles of water at 298 K and 5 atm pressure of air.

Solution:

$P_{gas} = K_H \times X_{gas}$

$$5 \times 0.8 = \frac{10^5 \times n_{N_2}}{(n_{N_2} + n_{H_2O})}$$

$$\boxed{n_{N_2} = 4\times10^{-4}}$$

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BEGINNER'S BOX-4

1. Which of the gas will not follow Henry's law?
(1) HCl (2) He (3) O_2 (4) H_2

2. If solubility of gas 'X' is 0.5 gL^{-1} at 1 bar then its solubility at 3 bar pressure will be
(1) 0.5 gL^{-1} (2) 1.5 gL^{-1} (3) 3.0 gL^{-1} (4) 2 gL^{-1}

3. Among the following that forms an ideal solution?
(1) Water and methanol (2) Acetone and ethanol
(3) Benzene and toluene (4) Water and HCl

4. On mixing 10 mL of acetone with 40 ml of chloroform the total volume of the solution is
(1) < 50 mL (2) > 50 mL (3) = 50 mL (4) cannot be predicted

5. The mixture of n-hexane and n-heptane is an example of
(1) Ideal solution (2) Non-ideal solution (3) Dilute solution (4) None

BEGINNER'S BOX ANSWERS KEY

BEGINNER'S BOX-1	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	3	3	1	3	3	2	4	1	2	1

BEGINNER'S BOX-2	Que.	1	2	3	4	5
	Ans.	4	2	3	2	3

BEGINNER'S BOX-3	Que.	1	2	3	4
	Ans.	3	1	2	2

BEGINNER'S BOX-4	Que.	1	2	3	4	5
	Ans.	1	2	3	1	1

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